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(54) POLYESTER RESIN SHEET AND ITS PRODUCTION

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a polyester resin sheet having embossed patterns applied to the surface thereof, excellent in light diffusibility and reduced in the disappearance of the embossed patterns after thermal molding.
SOLUTION: A polyester resin sheet comprises a resin compsn. wherein white fine particles are compounded with a polyester resin and is a substantially amorphous non-oriented sheet and embossed patterns are applied to at least one surface of this sheet and the surface glossiness of the sheet is is 60% or less and 70% or less after 20 sec heat treatment at 120° C. The substantially amorphous non-oriented sheet comprising the resin compsn. wherein the white fine particles are compounded with the polyester resin is held between a pair of rolls at least one of which is the embossing roll and the surface temp. of the embossing roll is set to 110-170° C and embossed patterns are applied to at least one surface of the sheet to produce the polyester resin sheet.

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CLAIMS

[Claim(s)]
[Claim 1]Consist of a resin composite in which white particles were blended with polyester resin, and are a sheet for undivided of amorphous state substantially, and an embossed pattern is given to at least one surface, and. A polyester resin sheet, wherein a degree of brilliancy of this surface is 60% or less and a degree of brilliancy of this surface after heat treatment for 20 seconds is 70% or less at 120 **.
[Claim 2]The polyester resin sheet according to claim 1 whose total light transmittance is not less than 40%.
[Claim 3]The polyester resin sheet according to claim 1 or 2 whose Hays is not less than 70%.
[Claim 4]The polyester resin sheet according to any one of claims 1 to 3 whose main composition repeating unit of polyester resin is ethylene terephthalate.
[Claim 5]The polyester resin sheet according to any one of claims 1 to 4 whose polyester resin is amorphous resin substantially.
[Claim 6]The polyester resin sheet according to any one of claims 1 to 5 whose white particle in a resin composite is silicone resin.
[Claim 7]The polyester resin sheet according to any one of claims 1 to 6 whose blending ratio of white particles in a resin composite is 0.1 to 20 weight %.
[Claim 8]Consist of a resin composite in which white particles were blended with polyester resin, and pinch a sheet for undivided of amorphous state substantially between rolls of a couple which used at least one side as an embossing roll, and. A manufacturing method of a polyester resin sheet giving an embossed pattern for skin temperature of this embossing roll to at least one surface of a sheet as a range of 110-170 **.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention about a polyester resin sheet and a manufacturing method for the same in more detail, An embossed pattern is given to the surface and it excels in light diffusibility, and there is little disappearance of the embossed pattern after thermoforming, and it is related with an illuminating cover, a polyester resin sheet suitable as various ornaments or materials for a display, and a manufacturing method for the same as an anti-dazzle outstanding thermoforming object, for example.
[0002]
[Description of the Prior Art]Conventionally the polyester resin represented by polyethylene terephthalate resin, In addition to outstanding mechanical properties and chemical property, extrusion molding is observed and carried out from fields, such as the outstanding transparency, gas barrier properties, and safety-and-hygiene nature, and remarkable elongation is shown in the various application as a film, a sheet, etc. And the film is manufactured by usually extending and carrying out orientation of the sheet made into the crystallized state extruded to the sheet shaped to one axis or two axes from an extrusion machine.
On the other hand, in order to make subsequent thermoforming etc. easy, after extruding a sheet from an extrusion machine to a sheet shaped, it is quenched, and is usually substantially manufactured as a sheet for undivided of amorphous state.

[0003]About the sheet for undivided of this amorphous state, by blending white particles with base material polyester resin, this invention persons gave light diffusibility and proposed the anti-dazzle property sheet useful as an illuminating cover etc. in the place (Tokuganhei8-203681, Tokuganhei9-74025). The attached embossed pattern disappeared at the time of thermoforming, and this invention persons faced the problem that light diffusibility and anti-dazzle improvement was not accepted as a thermoforming object, as a result of examining how to give an embossed pattern to a sheet surface for the purpose of the further light diffusibility improvement.
[0004]
[Problem to be solved by the invention]This invention was made for the purpose of solving the problem of disappearance of the embossed pattern at the time of the above-mentioned thermoforming, and this invention is the polyester resin sheet in which the embossed pattern was given to the surface. The purpose is excellent in light diffusibility, and it is providing a polyester resin sheet with little disappearance of the embossed pattern after thermoforming, and a manufacturing method for the same.

[0005]
[Means for solving problem]It is what traced that the temperature of resin when an embossed pattern is attached on the surface of a polyester resin sheet was important as a result of inquiring wholeheartedly that this invention persons should attain said purpose, and completed this invention, Namely, this invention consists of a resin composite in which white particles were blended with polyester resin, and are a sheet for undivided of amorphous state substantially, and the embossed pattern is given to at least one surface, and. The polyester resin sheet whose degree of brilliancy of this surface after heat treatment for 20 seconds the degree of brilliancy of this surface is 60% or less, and is 70% or less at 120 **, And consist of a resin composite in which white particles were blended with polyester resin, and pinch the sheet for undivided of amorphous state substantially between the rolls of the couple which used at least one side as the embossing roll, and. Let the manufacturing method of the polyester resin sheet which gives an embossed pattern for the skin

temperature of this embossing roll to at least one surface of a sheet as a range of 110-170 ** be a summary.

[0006]

[Mode for carrying out the invention]In this invention, as polyester resin which constitutes a resin composite, A polycondensation body with a diol unit which uses as the main ingredients a dicarboxylic acid unit which uses terephthalic acid or its alkyl (about one to four carbon number) ester as the main ingredients, and ethylene glycol from fields, such as economical efficiency and recycling efficiency, That is, that whose main composition repeating unit is ethylene terephthalate is preferred. In inside, a rate of a terephthalic acid unit over all the dicarboxylic acid units More than 80 mol %. It is preferred more than 90 mol % and that it is more than 95 mol % especially, and more than 50 mol % and also more than 60 mol %, and that it is more than 65 mol % especially have a preferred rate of ethylene glycol units over all the diol units.

[0007]As a copolymer component, as dicarboxylic acid units other than terephthalic acid and its alkyl ester, For example, phthalic acid, isophthalic acid, 4,4'-diphenyldicarboxylic acid, 4,4'-difenoxicarboxylic acid, 4,4'-diphenyl ether dicarboxylic acid, Aromatic dicarboxylic acid, such as 4,4'-diphenylsulfone dicarboxylic acid, 2, and 6-naphthalene dicarboxylic acid, Alicyclic dicarboxylic acid, such as hexahydro terephthalic acid and hexahydro isophthalic acid, A kind of aliphatic dicarboxylic acid, such as malonic acid, succinic acid, adipic acid, azelaic acid, and sebacic acid, or two sorts again as diol units other than ethylene glycol, For example, propylene glycol, a trimethylene glycol, tetramethylene glycol, Pentamethylene glycol, hexamethylene glycol, a decamethylene glycol, Alicyclic diol, such as aliphatic series diol, such as neopentyl glycol and a diethylene glycol, 1,3-cyclohexane dimethanol, and 1,4-cyclohexane dimethanol, 4,4'-dihydroxybiphenyl, 2,2-bis(4'-hydroxyphenyl) propane, Kinds, such as aromaticdiol, such as 2,2-bis(4'-beta-hydroxyethoxyphenyl)propane, a bis(4-hydroxyphenyl)sulfone, and bis(4-beta-hydroxyethoxyphenyl)sulfonic acid, or two sorts or more are used, respectively. For example, hydroxycarboxylic acid and alkoxy carboxylic acid, such as para-hydroxybenzoic acid and p-beta-hydroxyethoxybenzoic acid, And copolymerization of a little polyfunctional ingredients of three or more organic functions, such as monofunctional ingredients, such as stearic acid, benzoic acid, stearyl alcohol, and benzyl alcohol, trimellitic acid, pyromellitic acid, bird methanol ethane, and pentaerythritol, etc. may be carried out.

[0008]In this invention, especially a desirable thing in said polyester resin, A main composition repeating unit is ethylene terephthalate, and Isophthalic acid, It is the copolymerized polyester resin of 2,6-naphthalene-dicarboxylic-acid, diethylene-glycol or 1, and 4-cyclohexane dimethanol which made a kind a copolymer component at least, Also in it, what is amorphism nature substantially is the most preferred from fields, such as mechanical properties, such as sheet forming nature, embossing nature, and shock resistance. What is antimony and germanium as a metallic element which originates in a catalyst at the time of a polycondensation, and is contained from fields, such as a color tone of a sheet and thermal stability, is preferred.

[0009]As white particles which constitute a resin composite, inorganic particles, such as organic particulates, such as silicone resin, calcium carbonate, barium sulfate, titanium oxide, and silica, etc. are mentioned, and silicone resin and barium sulfate are preferred in inside. As for such mean particle diameter, it is preferred that they are 0.5-5 micrometers and also 1-4 micrometers in fields, such as the light diffusibility of a sheet and light transmission, to primary particle diameter. As for a blending ratio of this white particle in a resin composite, it is preferred 0.1 to 20 weight % and also that it is 1 to 10 weight % especially 0.5 to 15weight %. It becomes a tendency which is inferior in the light diffusibility of a sheet, and becomes the tendency for light transmission of a sheet and a moldability, shock resistance, etc. to fall, by said excess of the range at said less than range.

[0010]Other resin, such as polycarbonate system resin, polyamide system resin, and polyolefin system resin, may be blended with the polyester resin composition in this invention in the range which does not spoil the effect of this invention, for example, and the loadings in that case are made into 20 or less weight %. The additive agent used for the usual resin composites, such as an antioxidant, an ultraviolet ray absorbent, a spray for preventing static electricity, an antiblocking agent, fire retardant, colorant, and a fluorescence agent, may be added by the polyester resin composition in this invention.

[0011]On the real target which consists of said polyester resin composition, if the polyester resin sheet of this invention needs to be a sheet for undivided of amorphous state and is a crystallized state, It becomes that in which optical properties, such as the light diffusibility of a sheet, and a moldability, shock resistance, etc. are inferior, and the moldability of a sheet, etc. are inferior even if it is carrying out orientation.

[0012]Substantially here the sheet for undivided of amorphous state, With a conventional method, the masterbatch which made said polyester resin contain said white particle in about 10 to 50weight % of high concentration, for example, Supply, dilute with said polyester resin, carry out melt kneading to an extrusion machine, and so that white particles may serve as a desired blending ratio A resin composite and nothing, After extruding this resin composite from an extrusion machine to a sheet shaped with the resin temperature of 250-320 **, the skin temperature of 0-80 ** preferably on a 10-50 ** casting roll, It can manufacture by carrying out quenching solidification, sticking a sheet on a casting roll by a touch roll.

[0013]In this invention, saying above-mentioned "it is an unextended sheet of amorphous state substantially." It can check according to the theoretical amorphism density which says the state where the heat history and/or the extension history are not received after quenching solidification is carried out by the method like the above-mentioned for example, by which the density of a sheet is computed from the amorphism density of raw material polyester resin, and the density of other raw materials, and a substantially equivalent thing.

[0014]In this invention, the limiting viscosity of the polyester resin composition [in / substantially / said sheet for amorphous state and undivided] which consists of said polyester resin composition, 0.25 g of samples are dissolved in the mixed solvent 25g of phenol/1,1,2,2-tetrachloroethane (weight ratios 1/1), The limiting viscosity measured at 30 ** is 0.60 or more dl/g, it is preferred that 0.63 or more dl/g is 0.65 or more dl/g especially, and it is usually 0.90 or less dl/g.

[0015]The embossed pattern is given to at least one surface, and the polyester resin sheet of this invention. The degree of brilliancy of this surface is 20% or less especially preferably 30% or less still more preferably 40% or less preferably 60% or less, The degree of brilliancy of this surface after heat treatment for 20 seconds at 120 ** And 70% or less, Preferably, 50% or less, it is 30% or less preferably, and in the degree of brilliancy of an embossed pattern side, the embossed pattern after thermoforming will disappear in said excess of the range, and the light diffusibility and anti-dazzle outstanding thermoforming object will be acquired especially 40% or less still more preferably.

[0016]The polyester resin sheet which has said degree of brilliancy of this invention, Said sheet for amorphous state and undivided is substantially pinched between the rolls of the couple which used at least one side as the embossing roll, and the skin temperature of this embossing roll can be manufactured by giving an embossed pattern to at least one surface of a sheet as a range of 110-170 **. Here, it becomes difficult only for the sheet that an embossed pattern disappears to be obtained when the skin temperature of an embossing roll considers it as a thermoforming object in said less than range, and to give an embossed pattern to a sheet in said excess of the range itself.

[0017]Said embossing may be performed using the remaining heat at the time of extrusion using the roll which performed embossing to the casting roll or the touch roll according to the publicly known method at the time of said extrusion sheet manufacture conventionally, Once establishing independently the embossing process which installed the embossing roll, making said extrusion sheet manufacture follow, carrying out with in-line one and rolling round said extrusion sheet, it may rewind and may carry out off-line.

[0018]When hard chrome plating is given to the surface, and what made the surface roughness the uneven shape of 0.5-5S is used preferably and an embossing roll circulates the skin temperature for temperature control oil etc. inside a roll, It is preferred to consider it as the range of 125-150 ** still more preferably, and to abbreviated-coincide this roll temperature and the sheet temperature at the time of the end of embossing 120-160 ** preferably, 110-170 **. As for especially the contact time of the sheet at the time of embossing, and an embossing roll, it is preferred 10 to 40 seconds and also to consider it as 15 to 30 seconds for 13 to 35 seconds.

[0019]It has preferred total light transmittance not less than 40% and also that it is not less than 50% especially not less than 45%, and the polyester resin sheet of this invention has [not less than 70% and also that it is not less than 85% especially not less than 80%] still more preferred Hays. Here, total light transmittance and Hays are the measured value in the method specified to JIS K7105.

[0020]As for the thickness of the polyester resin sheet of this invention, it is usually preferred from fields, such as mechanical properties, such as optical properties, such as light transmission, and shock resistance, 0.1-5 mm and also that it is 0.3-2 mm especially 0.2-3 mm.

[0021]a bilayer layered product with the other resin which the polyester resin sheet of this invention is a monolayer, and gave the various function, for example, such as polyester resin or an acrylic resin, -- or, As three layers which used the polyester resin sheet of this invention for both the surface layer by making these resin into an intermediate layer, or a multilayer layered product beyond it, thermoforming is carried out by vacuum forming method, a pressure-forming method, etc., for example, it is suitably used as an illuminating cover, and various ornaments and the materials for a display.

[0022]

[Working example]Hereafter, although an embodiment explains this invention still in detail, this invention is not limited to the following embodiments, unless the summary is exceeded.

As embodiment 1 polyester resin, an ethylene terephthalate unit occupies 100% of composition repeating units (in addition). The diethylene glycol which carries out a byproduction at the time of a polymerization is also counted as ethylene glycol. Using polyethylene terephthalate resin (limiting viscosity 0.71 dl/g, the Mitsubishi Chemical make, "GS400"), as white particles, Using spherical silicone resin (the mean particle diameter of 2 micrometers, the Toshiba Silicone make, "toss pearl 120"), the masterbatch which made polyester resin contain silicone resin 20weight % was diluted with polyester resin so that the blending ratio of silicone resin might be 1.5 weight %.

[0023]Supply a twin screw extruder with a diameter of 40 mm which has three vent ports where said masterbatch and resin were connected to the depressurizing system of 1mmHg as an object for intermediate layers, and, on the other hand, as an object for both surface layers, After supplying and carrying out melt kneading to a twin screw extruder with a diameter of 30 mm which has two vent ports where said masterbatch and resin were connected to the depressurizing system of 1mmHg and making with a resin composite, each is supplied to the co-extrusion-molding machine provided with the T die, The three-layer lamination layer sheet for undivided of amorphous state was fabricated on the with 0.8 mm in thickness of an intermediate layer, each 0.1 mm in thickness of a surface layer, and an overall thickness of 1 mm real target by carrying out a co-extrusion to the two-sort shape of a multilayer sheet of three layers, and quenching on the casting roll set as 30 **. As for the degree of brilliancy of the surface of this three-layer lamination layer sheet, Hays of light transmission was 92% 60% 98%.

[0024]Then, the preheating roll by which temperature control was carried out to 80 ** with the diameter of 300 mm in the obtained three-layer lamination layer sheet, The embossing roll by which hard chrome plating of the surface roughness 2S was given to the surface with the equal diameter, and temperature control was carried out to 110 **, It pinched between each roll which the touch roll by which temperature control was carried out to 70 ** with the equal diameter is arranged lengthwise, and rotates by a part for peripheral velocity/of 1.4 m, and the polyester resin sheet to which the embossed pattern was given on the surface of one side was manufactured preheating and by carrying out embossing. The contact time with the embossing roll of the sheet in this case was about 20 seconds. About the polyester resin sheet to which the acquired embossed pattern was given, it measured, a degree of brilliancy, the disappearance state of the embossed pattern after heat treatment and a degree of brilliancy, light transmission, and Hays were evaluated by the method shown below, and the result was shown in Table 1.

[0025]About the sample (5 cm x 5 cm) started from the degree-of-brilliancy sheet, specular gloss was measured 60 degrees based on JIS K7105 using the Horiba glossmeter.

The sample (5 cm x 5 cm) started from the disappearance state sheet of the embossed pattern after heat treatment, After neglecting it for 20 seconds and heat-treating by an air atmosphere in the automatic oven for polymer (the product made by DR.STAPFER, "Metra Corp stat IR400") set as 120 **, visual observation of the disappearance state of an embossed pattern was carried out, and the following standards estimated.

O; most disappearance is not accepted.

**; although there is no disappearance, the embossed pattern is crushed as compared with heat treatment before.

x; disappearance is remarkable.

[0026]About the sample heat-treated by the same method as the degree-of-brilliancy above after heat treatment, the degree of brilliancy was measured by the same method as the above.

About the thickness direction of the sample (5 cm x 5 cm) started from the light transmission sheet, it measured based on JIS K7105 using the Suga Test Instruments hazemeter.

About the thickness direction of the sample (5 cm x 5 cm) started from the Hays sheet, it measured based on JIS K7105 using the Suga Test Instruments hazemeter.

[0027]The outside which changed the skin temperature of one to Embodiments 2-4 and comparative example 2 embossing roll as shown in Table 1, A degree of brilliancy, the disappearance state of the embossed pattern after heat treatment and a degree of brilliancy, light transmission, and Hays were measured and evaluated about the sheet obtained by manufacturing the polyester resin sheet to which the embossed pattern as well as Embodiment 1 was given, and the result was shown in Table 1.

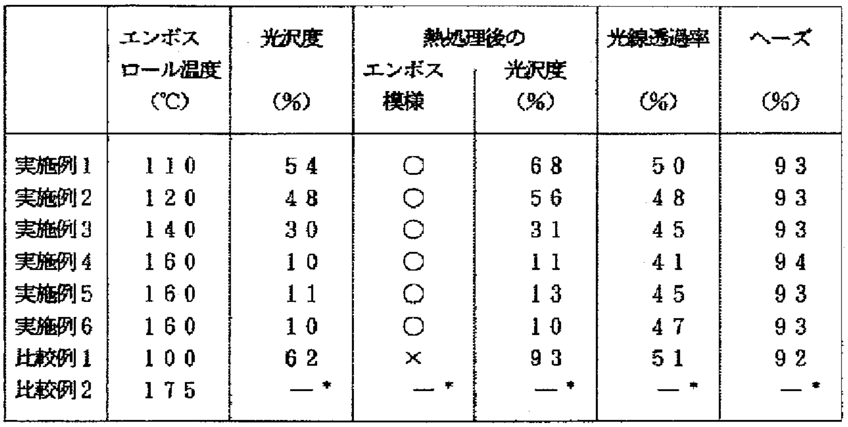
[0028]A dicarboxylic acid unit as polyester resin for five embodiments surface layers 100 mol of terephthalic acid %, A diol unit Ethylene glycol 70 mol % (in addition, the diethylene glycol which carries out a byproduction at the time of a polymerization is also included.), the polyethylene terephthalate copolymer resin (limiting viscosity -- 0.82 dl/g) of amorphism nature in which it is 1,4-cyclohexane dimethanol 30 mol %, and an ethylene terephthalate unit occupies 70-mol% of composition repeating units The outside which changed the skin temperature of the embossing roll as shown in Table 1 made in Eastman Chemical and using "PETG", A degree of brilliancy, the disappearance state of the embossed pattern after heat treatment and a degree of brilliancy, light transmission, and Hays were measured and evaluated about the sheet obtained by manufacturing the polyester resin sheet to which the embossed pattern as well as Embodiment 1 was given, and the result was shown in Table 1.

[0029]As polyester resin for embodiment 6 intermediate layer and for both surface layers, the polyethylene terephthalate copolymer resin of the same amorphism nature is used with having used in Embodiment 5, The outside which changed the skin temperature of the embossing roll as shown in Table 1, A degree of brilliancy, the disappearance state of the embossed pattern after heat treatment and a degree of brilliancy, light transmission, and Hays were measured and evaluated about the sheet obtained by manufacturing the polyester resin sheet to which the embossed pattern as well as Embodiment 1 was given, and the result was shown in Table 1.

[0030]

[Table 1]

表1



	エンボスロール温度 (℃)	光沢度 (%)	熱処理後の エンボス模様	熱処理後の 光沢度 (%)	光線透過率 (%)	ヘーズ (%)
実施例1	110	54	○	68	50	93
実施例2	120	48	○	56	48	93
実施例3	140	30	○	31	45	93
実施例4	160	10	○	11	41	94
実施例5	160	11	○	13	45	93
実施例6	160	10	○	10	47	93
比較例1	100	62	×	93	51	92
比較例2	175	—*	—*	—*	—*	—*

* エンボスロールに付着してサンプル得られず、評価不可。

[0031]

[Effect of the Invention]According to this invention, it is the polyester resin sheet in which the embossed pattern was given to the surface, and it excels in light diffusibility and a polyester resin sheet with little disappearance of the embossed pattern after thermoforming and a manufacturing method for the same can be provided.

[Translation done.]